DESULFURIZATION AND DEMINERALIZATION OF COAL BY MOLTEN NaOH/KOH MIXTURES

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INTRODUCTION

The use of molten caustic to remove pyrite and other mineral matter from coal was first reported by Masciantonio (1). He discovered that treating 1 part of coal with 4 parts of 1:1 NaOH/KOH mixture at 250°C or higher removed all of the pyrite within 5 minutes. At temperatures above 250°C, organic sulfur was also removed. In recent years, the technique was refined by TRW and became known as the Gravimelt Process (2-4). By using 10 parts of molten caustic to treat 1 part of coal at 370°C, followed by washing with dilute H_2SO_4, almost all of the pyritic sulfur and about 80% of the organic sulfur could be removed. In addition, the final ash contents were generally less than 1%. Further studies on the effects of retention time, temperature, coal-to-caustic and NaOH/KOH ratios, particle size, and rank of coal resulted in sulfur and ash reductions which met the New Source Performance Standards (5,6). The fundamental aspects of cleaning coal with molten caustic were also studied by Maijgren et al. (7, 8) who investigated the behavior of some organosulfur model compounds in addition to the effect of caustic composition, reaction time, temperature, and particle size.

The overall objectives of our own DOE-sponsored work at the Ames Laboratory are to propose, test, and develop methods for regenerating the spent caustic and other reagents used in the TRW Gravimelt Process in order to make this chemical cleaning method economical. As a preliminary step to our investigations, the thermodynamics, phase equilibria, and other properties of proposed reaction schemes were tested in order to develop flow diagrams incorporating the desulfurization and regeneration schemes (9). Furthermore, in order to ensure that our samples of cleaned coal and spent caustic are comparable to those produced by the Gravimelt Process, similar procedures were used in the cleaning steps. In the course of our work, the effect of various washing procedures as well as of particle size and recleaning was investigated. In addition, some fundamental chemistry and behavior of the mineral matter during cleaning were studied on our own samples and on samples provided by TRW.

EXPERIMENTAL

For our own work, channel samples of Pittsburgh No. 8 coal from the Grafton Mine, Churchville, WV, and Illinois No. 6 from the Captain Mine, Percy, IL, were used. Two separate batches, IL6 and IL6A, of the Illinois coal were used. The characteristics of the 2 bituminous coals are listed in Table 1.

The desulfurization experiments were run in a batch reactor designed and constructed at Ames Laboratory. The reaction crucible (8 in. x 3.5 in. o.d.) was constructed from Inconel tubing. A basket to hold the coal was fashioned from 20 mesh stainless steel screen. The chromel-alumel thermocouple was sheathed in stainless steel.

* Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

Table 1. Analyses for Pittsburgh No. 8 (PT8) and Illinois No. 6 (IL6 and IL6A) Coal (on a dry basis, except for moisture)

	% H_2O	% Ash	% S	(Pyr.	Sulf.	Org.)	% V.M.	H.V., Btu/lb
PT8	2.18	7.02	3.12	(1.48	0.26	1.38)	39.27	13,482
IL6	8.25	13.26	4.10	(1.82	0.29	1.99)	36.55	11,833
IL6A	8.70	14.17	4.52	(2.21	0.23	2.08)	38.50	12,245

For the experiments, 50g of coal (usually 12 x 0 mesh) were placed in the basket and covered with 400g NaOH and 100g KOH. The basket, thermocouple, and stirring rod were placed in the crucible, and the crucible was lowered into the preheated furnace. The coal-caustic mixture was stirred and kept at 370°C for 1 hour while a continuous flow of nitrogen above the crucible provided an inert atmosphere. After the reaction, the basket containing the coal cake was removed from the reactor. The cake contained about 2 parts of caustic adhering to 1 part of coal by weight. The cake was first washed with 2L of water, followed by 1L of 10% H_2SO_4 or HCl, and then a final wash with 2 or 4L water.

The cleaned coal was dried at 110°C overnight and then sampled for analysis. Moisture, ash, and pyritic and sulfate S were determined by ASTM procedures (10). Total S was determined by high-temperature combustion using a Fisher Total Sulfur Analyzer. Organic sulfur was determined by difference.

For comparison, samples of another Pittsburgh No. 8 coal were obtained in March, 1983, from the TRW Gravimelt Benchscale Run #2 performed in California. The samples included raw coal, water-washed caustic-treated coal (intermediate product), and the final clean product (after additional acid and water wash) from the Gravimelt Process. In addition to the standard analyses described above, the samples were also analyzed directly for organic sulfur by a technique utilizing scanning electron microscopy (SEM) and energy-dispersive x-ray spectrometry as described by Straszheim et al. (11). Furthermore, they were characterized for various mineral phases and their distribution among different particle sizes by SEM and automated image analysis (SEM-AIA), a technique described previously by Straszheim and Markuszewski (12).

RESULTS AND DISCUSSION

Standard Conditions

The results for several cleaning experiments on the Pittsburgh No. 8 (PT8) and Illinois No. 6 (IL6 or IL6A) coals are presented in Table 2. For the Pittsburgh coal, under standard conditions (runs #3 and #16), 77-82% ash removal and 65-72% sulfur removal were achieved with recoveries around 85-90%. For the Illinois coal, (IL6 #6, IL6A #1, and IL6A #2), the ash and sulfur removal were better at 87-89% and 72-78%, respectively, while recoveries were lower at 75-79%.

Better Washings

When more water was used for the washing step (PT8 #10) and when the wash water

Table 2. Removal of Sulfur and Ash from Pittsburgh (PT8) and Illinois (IL6 or IL6A) Coals Under Standard[1] or Modified Conditions

Sample Run #	Conditions[1]	% H_2O	% Ash[2]	% Removal	% S[2]	% S Removed	% Rec.[3]
PT8	Untreated	2.18	7.02	----	3.12	----	----
PT8 #3		0.01	1.27	82.4	1.09	65.1	89.7
PT9 #9	Same as #3, but 10% HCl wash	0.16	2.27	67.6	0.91	70.8	87.9
PT8 #10	4L Wash	0.08	1.50	78.6	0.87	72.1	89.6
PT8 #12	4L Hot Wash	0.22	1.07	84.8	0.68	78.5	91.0
PT8 #16		0.18	1.61	77.0	0.89	71.5	84.6
PT8 #13	#10 recleaned	0.17	0.30	95.8	0.38	87.8	72.8 (overall) 81.1 (2nd step only
IL 6	Untreated	8.25	13.26	----	4.10	----	----
IL 6 #6	+60 mesh (80%)	0.33	1.79	86.5	1.16	71.7	74.5
IL6 #10	-60 mesh (85%)	0.48	0.56	95.8	0.57	86.1	64.7
IL6A	Untreated	8.70	14.17	----	4.52	----	----
IL6A #1		0.29	1.85	86.9	1.01	77.7	79.12
IL6A #2		0.25	1.53	89.2	1.12	75.2	79.12

[1] Standard conditions are: 10:1 caustic/coal ratio, 4:1 NaOH/KOH ratio, 370°C for 1 hour, 2L hot water (100°C) wash, 1L 10% H_2SO_4 wash (60°C), 4L hot H_2O wash (100°C). Only nonstandard conditions are listed.
[2] % Sulfur and % ash are reported on a dry basis.
[3] % Recovered = % $\frac{\text{grams MAF coal out x 100}}{\text{grams MAF coal in}}$

was heated to 100°C (PT8 #12), both ash and sulfur removals were improved for each step without appreciable decrease in recovery.

Different Acid

When 10% HCl was substituted for 10% H_2SO_4 (PT8 #9), the sulfur removal was improved, but the ash removal was worse than for run PT8 #3 in which 10% H_2SO_4 was used.

Recleaning

Best results were obtained when cleaned coal from run PT8 #10 was cleaned again under the same conditions. The final ash content of 0.30% and final sulfur content of 0.38% represent removals of 96 and 88%, respectively. The overall recovery, however, decreased to 73%. The lower recovery may be due partially to increased handling and the associated mechanical losses.

Finer Grind

The 12 x 0 mesh IL6 coal, sized as 80% plus 60 mesh, was used in run #6. When the sample was ground to 85% minus 70 mesh and used in run #10, the final ash content of 0.56% and final sulfur content of 0.57% achieved represent significant improvements in removal, to 96% and 86%, respectively. The lower recovery of 65% can again be attributed in part to mechanical losses of the finer coal through the mesh of the basket.

Effect of Various Washings on Sulfur Forms

The decrease in the total sulfur content of cleaned PT8 coal was followed by observing the various sulfur forms after different washing procedures. Results of these analyses are presented in Table 3. Use of a 2L wash under standard conditions (run #3) showed an appreciable residue of sulfate in the cleaned coal, greater than the amount of sulfate present in the original, untreated coal. Such incorporation of sulfate after treatment with H_2SO_4 has been observed before in our laboratories (13). It may be due to the formation of organic sulfate esters or formation of inorganic sulfates or some other mechanism for adding sulfate. When more thorough washing was used in run #10, the sulfate content was decreased significantly. When 10% HCl was used for the acid wash in run #9, there was no chance of sulfate incorporation and thus the final sulfate content was almost zero.

Table 3. Effect of Washing Improvements on Sulfur Forms

Sample Run #	Conditions	% Pyritic Sulfur	Sulfatic Sulfur	Organic Sulfur	Total Sulfur
PT8	Untreated	1.48	0.26	1.38	3.12
PT8 #3	Standard 2L wash	0.02	0.47	0.60	1.09
PT8 #9	10% HCl wash	0.06	0.02	0.83	0.91
PT8 #10	4L wash	0.01	0.13	0.73	0.87

Effect of Molten Caustic on Particle Size

The Pittsburgh No. 8 coal used in run #3 was sized using sieves and a portable sieve shaker before and after the molten caustic treatment. The results of the sieve analyses are presented in Table 4. For the untreated coal, 20.1% of the particles were -60 mesh. After the treatment, 38.6% of the coal particles were -60 mesh, indicating severe comminution of the sample by action of the molten caustic. When the same cleaned and sieved sample was sieved again, the -60 mesh fraction increased to 44.4% indicating that the treated coal particles were friable and continued to break down further by even simple sieving. When the raw coal was sieved for a second time, results showed that the particle size distribution was unaffected. The degradation of coal matter by molten caustic can occur by pitting due to removal of mineral grains as well as by direct attack on the coal macerals. Observations of such attacks have been made by Oder et al. (14) on samples prepared by TRW. In addition, sudden release of moisture and volatile matter during contact with molten caustic can also contribute to the comminution process.

Effect of Gravimelt Process on Mineral Matter in Coal

The samples of Pittsburgh No. 8 coal obtained from TRW, representing raw coal, the intermediate product and the final cleaned coal, were analyzed by ASTM and other procedures. The results are presented in Table 5. In the final product, the total and organic sulfur were reduced by 70-80% from the levels observed in the raw coal, and the pyritic sulfur was reduced by about 99%, while levels of sulfate sulfur were

Table 4. Sieve Analysis for Pittsburgh No. 8 Coal Before and After Cleaning With Molten Caustic at Ames Laboratory

	RAW COAL		CLEAN COAL	
Mesh Size	PASS #1 Wt. %	PASS #2 Wt. %	PASS #1 Wt. %	PASS #2 Wt. %
>12	15.0	14.6	4.5	3.3
12-60	65.0	65.6	56.9	52.2
60-120	9.8	9.8	20.6	24.9
120-170	3.2	3.1	5.0	5.9
170-200	1.2	1.2	1.9	2.2
200-325	2.7	2.7	4.7	5.2
<325	3.2	3.0	6.4	6.2

Table 5. Analysis of Raw and Gravimelt Treated Pittsburgh No. 8 Coal. Values are in % unless otherwise noted and, except for moisture, are corrected to a dry basis).

	RAW			INTERMEDIATE PRODUCT			FINAL PRODUCT		
	TRW Data[a]	Ames Data	Org. S, by SEM[b]	TRW Data	Ames Data	Org. S, by SEM[b]	TRW Data	Ames Data	Org. S, by SEM[b]
Moisture	6.46	0.89	----	3.27	2.98	----	2.55	1.25	----
Ash	10.15	9.88	----	30.46	29.22	----	1.26	1.00	----
Total S	4.28	4.22	----	0.43	0.32	----	0.75	0.86	----
Pyritic S	2.20	1.78	----	----	0.02	----	----	0.01	----
Sulfate S	0.02	0.20	----	----	0.06	----	----	0.26	----
Organic S	2.06	2.24	1.99	----	0.24	0.08	----	0.59	0.41
Elemental S (ppm)	----	29	----	----	<1	----	----	4	----
Heat Value, BTU/lb	13,282	----	----	8,454	----	----	13,780	----	----
Mineral Matter[c]	12.50	12.00	----	----	33.03	----	----	1.13	----

[a] Analysis of head sample.
[b] Procedure in Reference 11.
[c] Mineral matter = (1.13 x ash) + (0.47 x pyritic S), as in Reference 12.

not significantly affected. The organic sulfur concentrations determined directly by the SEM technique were consistently lower than the indirect ASTM values. The deviation was most pronounced for the treated coals, which may indicate the formation of unusual minerals such as sulfides or jarosite during the Gravimelt process. Possibly, incomplete dissolution of pyrite in the ASTM method may also have inflated the ASTM organic sulfur values. These apparent discrepancies are being studied further. The magnitude of the reductions in levels of the various sulfur forms was generally better than the reductions for the Pittsburgh No. 8 coals observed at Ames Laboratory (see Tables 2 and 3).

In addition, the TRW samples were analyzed by the SEM-AIA technique described previously (12). The SEM-AIA data on the mineral phase identification and distribution between the size fractions are presented in Table 6 for all three samples of raw and treated coal. The SEM-AIA data show the nearly complete removal of many minerals and a reduction of more than 90% in the overall content of the coal as a result of the TRW Gravimelt Process. No major shifts in particle size distribution were observed, although the pyrite distribution shifted somewhat towards the coarse fraction after processing.

A significant change in mineralogy can be observed for the cleaned coals. The processed coals showed a much greater percentage of material classified as "miscellaneous" than did the raw coal, indicating formation of unusual minerals. For the washed, Gravimelt-treated coal, this miscellaneous portion contained significant amounts of Ca, K, and/or Na. SEM-EDX examination showed also a general enhancement of these cations in the coal rather than in a separate phase or in components enriched in these elements, indicating that they could be associated with the organic portion of coal (possibly with carboxylate or phenolate functions). Such enhancement of Ca ions in the organic portion of coal has been observed previously in coals after treatment by the Ames Oxydesulfurization Process (15) and in lower rank and severely weathered coals (16). In the final product from the Gravimelt treatment, the "miscellaneous" material contained appreciable amounts of Cr, Mn, and Ni or Fe (or both), suggesting contamination from nickel and stainless steel components. For many mineral categories, the relative weight percent decreased after the caustic treatment and then increased after the acid treatment. It appears that the caustic treatment altered much of the original mineral matter while forming unusual minerals. The iron-rich phase, for example, in the intermediate product could be $NaFeO_2$ which has been shown to be the principal product from the reaction of FeS_2 with fused NaOH (17). The subsequent acid treatment removed much of the unusual mineral matter in the "miscellaneous and unknown" category, thereby increasing the relative percentages in the other mineral categories.

CONCLUSIONS

Coal treated at Ames Laboratory with molten caustic by a procedure similar to that of the Gravimelt Process resulted generally in 80-90% reductions in ash and 70-80% reductions in total sulfur. The recoveries of coal on a moisture- and ash-free basis were 80-90%. The removal of sulfur and ash could be improved by better washing, finer grind, or additional cleaning. SEM-AIA data on samples treated by TRW showed the formation of unusual minerals in the treated samples, as well as enrichment of these minerals in certain elements. The decrease of 90% in the ash content could be explained by the removal of individual mineral phases in all particle sizes. Removal of organic sulfur was corroborated by a direct SEM-EDX technique.

ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Fossil Energy, Division of Coal Utilization, through the Pittsburgh Energy Technology Center, Coal Preparation Branch. The authors gratefully acknowledge Drs. R.A. Meyers and W.D. Hart at TRW Systems, for supplying samples of raw and chemically desulfurized coal on which our SEM-AIA analyses were performed.

Table 6. SEM-AIA Classification of Mineral Matter in Pittsburgh No. 8 Coal Samples Obtained from TRW. The mineral phases are described by chemistry and area-equivalent diameter (in μm), expressed as weight percent of the total coal.

Raw Coal

Mineral Phase	< 6.3	6.3-20	20-63	63-200	Total
	Particle size, μm				
Pyrite	0.25	1.67	1.63	0.96	4.50
Kaolinite	0.15	0.75	0.62	0.50	2.02
Illite	0.29	0.92	0.71	0.51	2.43
Quartz	0.13	0.58	0.25	0.37	1.32
Iron-rich	0.01	0.04	0.22	0.71	0.98
Calcite	0.00	0.00	0.01	0.00	0.01
Silicates	0.08	0.13	0.03	0.14	0.39
Misc. & Unknown	0.10	0.21	0.02	0.00	0.34
Total	1.01	4.30	3.50	3.19	12.00

Water-Washed Gravimelt-Treated Coal (Intermediate Product)

Mineral Phase	< 6.3	6.3-20	20-63	63-200	Total
	Particle size, μm				
Pyrite	0.13	0.18	0.08	0.00	0.40
Kaolinite	0.01	0.02	0.00	0.00	0.03
Illite	0.19	0.59	0.42	0.12	1.32
Quartz	0.01	0.07	0.00	0.00	0.08
Iron-rich	0.33	1.05	1.15	1.14	3.67
Calcite	0.05	0.07	0.00	0.00	0.11
Silicates	0.12	0.18	0.20	0.46	0.95
Misc. & Unknown	4.33	9.31	5.67	3.35	22.66
Total	5.17	11.46	7.53	5.07	29.22

Final Gravimelt Product

Mineral Phase	< 6.3	6.3-20	20-63	63-200	Total
	Particle size, μm				
Pyrite	.006	.010	.074	.173	.262
Kaolinite	.019	.054	.025	.154	.252
Illite	.023	.030	.008	.000	.060
Quartz	.023	.037	.014	.017	.091
Iron-rich	.004	.004	.000	.000	.008
Calcite	.003	.005	.002	.000	.010
Silicates	.007	.007	.003	.000	.017
Misc. & Unknown	.093	.147	.060	.000	.300
Total	.176	.295	.185	.343	1.000

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